PREPARATION OF 2,5-DISILYLATED THIOPHENE DERIVATIVES AND THEIR CONVERSION TO 2,5-DIHALO DERIVATIVES

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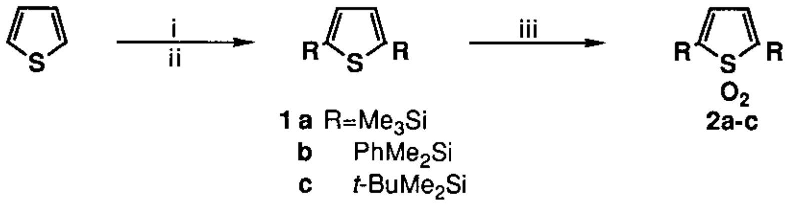
Abstract - 2,5-Disilylated thiophenes were prepared and readily oxidized with *m*-chloroperbenzoic acid (*m*-CPBA) to give the corresponding 1,1-dioxides. The thiophene dioxide was converted to 2,5-dihalogenothiophene dioxides with halogenating agents.

A few thiophene monooxides have been successfully isolated,[1] while dioxides bearing suitable substituents are isolated as stable compounds.[2] We have intended to explore the utilization of thiophene derivatives for organic synthesis and found that 2,5-bistrimethylsilyl and the related silyl derivatives were oxidized readily to give the corresponding sulfones. This paper reports the preparation and reactions of several silylated thiophene derivatives including silicon-bridged macrocycles.

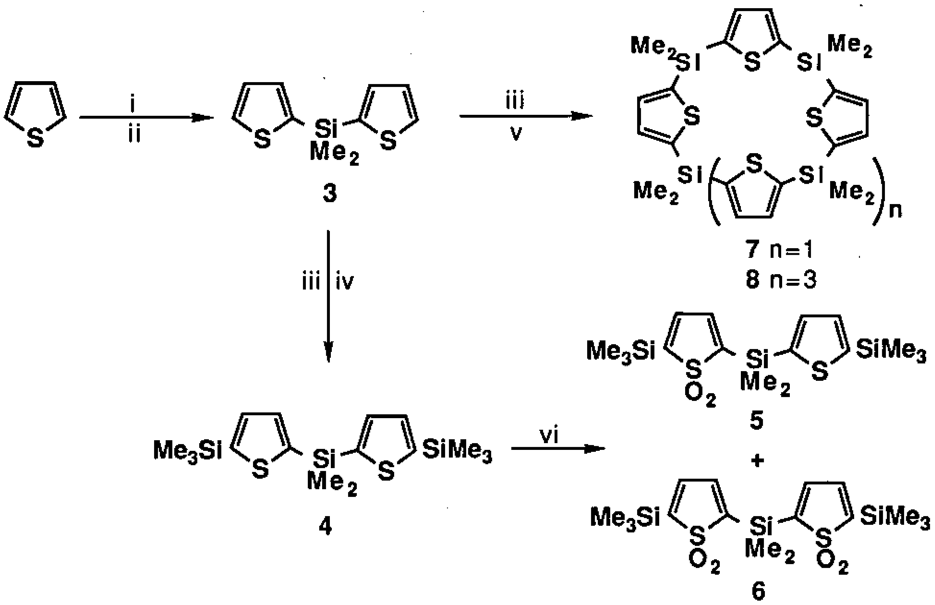
2,5-Disilylthiophenes (**1a-c**) were prepared by the known method[3] using 2 equivalents of BuLi and subsequent treatment of the dilithiothiophene with 2 equivalents of silyl chlorides. Then these were treated with *m*-CPBA to afford the corresponding sulfones (**2a-c**) in good yields (Scheme 1).[4]



Scheme 1. i. 2 eq. BuLi/THF/N_2/-20°C/1 h; ii. RCl/-20°C/1 h; iii. *m*-CPBA/CH_2Cl_2/room temperature/1 day

In a typical experiment, 2,5-bis(trimethylsilyl)thiophene (1a) (2.32 g, 10 mmol) was oxidized with *m*-CPBA (6.16 g, 25 mmol) in CH_2Cl_2 (200 ml) for 24 h at room temperature. After usual work-up and column chromatography using silica gel and hexane-CH_2Cl_2 (1:1) as an eluent, the crude crystals separated were recrystallized from hexane. 2,5-Bis(trimethylsilyl)thiophene 1,1-dioxide (2a) was obtained in 91% yield (Scheme 1). X-ray crystallographic analysis of **2a** reveals that it is a nearly planar molecule having a C_{2v} symmetry bisecting the SO_2 and the C_3-C_4 bond.[5]

When thiophene was treated with 1 equivalent of BuLi and then with 0.5 equivalent of dichlorodimethylsilane, dimethyldi(2-thienyl)silane (**3**) was obtained in 74% yield. **3** was treated with 2 equivalents of lithium diisopropylamide (LDA) and then with trimethylsilyl chloride affording dimethyl-bis-(5-trimethylsilyl-2-thienyl)silane (**4**) in 76% yield. In the oxidation of **4** with 1 equivalent of *m*-CPBA, one thiophene ring was preferentially oxidized to afford only the mono-sulfone (**5**) in 36% yield. For further addition of *m*-CPBA, the corresponding mono-sulfone (**5**) and bis-sulfone (**6**) were obtained in 21% and 41% yields, respectively.



Scheme 2. i. 1 eq. BuLi/THF/N_2/-20°C/1 h; ii. 0.5 eq. Me_2SiCl_2/-20°C/1 h;
iii. 2 eq. LDA/THF/N_2/-20°C/1 h; iv. 2 eq. Me_3SiCl/-20°C/1 h;
v. 1 eq. Me_2SiCl_2/-20°C/1 h;
vi. *m*-CPBA/CH_2Cl_2/room temperature/1 day

When the reaction of **3** was conducted by using 2 equivalents of LDA and 1 equivalent of dichlorodimethylsilane at -20 °C in THF for 2 h, macrocyclic compounds (**7**) and (**8**) were obtained without using high dilution technique. The products were separated by column chromatography (silica gel) and then purified by preparative liquid chromatography affording **7** and **8** in 17 and 15% yields, respectively.[6] Kauffman *et al.* reported the preparation of **7** in 16 % yield by similar procedure but using BuLi instead of LDA as a base.[7] However, judging from the physical and spectroscopic evidence, their product seems to be a mixture of **7** and **8**.

In order to convert these 1,1-dioxides to other thiophene derivatives, **2a** was treated with bromine or iodine in the presence of $AgBF_4$ in CH_2Cl_2 at 0 °C for 1 h to afford the corresponding bromo (**9**) and iodo (**10**) derivatives in 72 and 97 % yields, respectively.[8,9] When the reaction was carried out in the absence of $AgBF_4$, iodine did not react at all even changing the reaction conditions while bromine reacted with **2a** to give **9** in 47 % yield. But the reaction required high temperature (50 °C) and longer reaction time (72 h). The results are shown in Table 1.

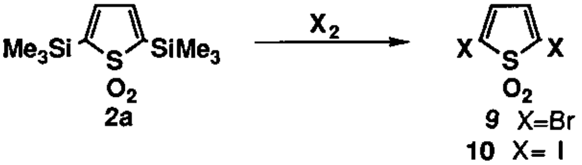


Table 1. Preparation of 2,5-Dihalogenated Thiophene 1,1-Dioxides

Run	X_2	Equiv.	Solvent	Temp. (°C)	Time (h)	Yield (%)
1	Br_2,$AgBF_4$[a)]	2	CH_2Cl_2	0	1	72
2	I_2,$AgBF_4$[a)]	2	CH_2Cl_2	0	1	97
3	Br_2	3	CCl_4	50	72	47
4	I_2	3	CCl_4	reflux	168	0

a) 3 eq. of $AgBF_4$ was used.

Introduction of silyl groups at the 2,5-positions in thiophene provides advantages not only for protection of the sulfonyl group from dimerization but also masking of the 2,5-positions of the thiophene ring to which halogen atoms can readily be introduced and hence promises to be a convenient method for preparation of various thiophene derivatives.

Further investigations on these thiophene dioxides and their derivatives are in progress.

ACKNOWLEDGEMENT

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4. **2a**: Yield, 91%; mp 153-154 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 6.74 (s, 2H, ThH), 0.34 (s, 18H, Me); ^{13}C-nmr ($CDCl_3$) δ 150.6, 135.9, -1.74; FT-ir (KBr) 1282, 1129 cm^{-1} (SO_2). Anal. Calcd for $C_{10}H_{20}O_2SSi_2$: C, 46.11; H, 7.74. Found: C, 46.05; H, 7.58; **2b**: Yield, 84%; mp 62-64 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 7.57-7.25 (m, 10H, ArH), 6.54 (s, 2H, ThH), 0.63 (s, 12H, Me); ^{13}C-nmr ($CDCl_3$) δ 149.6, 137.5, 134.5 134.0, 130.1, 128.1, -3.29; FT-ir (KBr) 1284, 1131 cm^{-1} (SO_2). Anal. Calcd for $C_{20}H_{24}O_2SSi_2$: C, 62.50; H, 6.25. Found: C, 62.41; H,6.24; **2c**: Yield, 80%; mp 154-155 °C (hexane); ^{1}H-nmr ($CDCl_3$) δ 6.80 (s, 2H, ThH), 0.99 (s, 18H, *t*-Bu), 0.31(s, 12H, Me); ^{13}C-nmr ($CDCl_3$) δ 149.1, 137.2, 26.3, 17.2, -6.02; FT-ir (KBr) 1284, 1127 cm^{-1} (SO_2). Anal. Calcd for $C_{16}H_{32}O_2SSi_2$: C, 61.54; H, 10.09. Found: C, 61.35; H, 10.18.
5. X-ray crystallographic analysis: bond lengths (Å); C-S:1.761, C_2-C_3(C_4-C_5):1.323, C_3-C_4:1.480. bond angles; O-S-O:113.4°, C_2-S-C_5:96.1°, C_2-S-O:111.5°.
6. **7**: mp 278-279 °C (lit.,[8] 224-226 °C); ^{1}H-nmr ($CDCl_3$) δ 7.39 (s, 8H, ThH), 0.63 (s, 24H, Me); ^{13}C-nmr ($CDCl_3$) δ 144.8, 135.5, -0.34; ms (m/z) 560 (M^+). Anal. Calcd for $C_{24}H_{32}S_4Si_4$: C, 51.38; H, 5.71. Found: C, 51.38; H, 5.61; **8**: mp 252-253 °C (benzene-hexane); ^{1}H-nmr ($CDCl_3$) δ 7.34(s, 12H, ThH), 0.63 (s, 36H, Me); ^{13}C-nmr ($CDCl_3$) δ 143.8, 136.6, -0.02; ms (m/z) 840 (M^+). Anal. Calcd for $C_{36}H_{48}S_6Si_6$: C, 51.38; H, 5.71. Found: C, 51.41; H, 5.73.
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8. The compound (**9**) has been synthesized by the oxidation of 2,5-dibromothiophene.[2c]
9. **10**: mp 147 -150 °C (decomp.) (dichloromethane-hexane); ^{1}H-nmr ($CDCl_3$) δ 6.87(s, 2H); ^{13}C-nmr ($CDCl_3$) δ 128.3, 119.3; ms (m/z) 368 (M^+); FT-ir (KBr) 1303, 1147 cm^{-1}(SO_2). Anal. Calcd for $C_4H_2O_2I_2S$: C, 13.04; H, 0.74. Found: C, 13.37; H, 0.74.

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